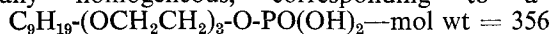


## Some properties of an oil-soluble phosphated fatty alcohol ethoxylate

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Although phosphated hydrocarbon ethoxylates are claimed to have properties associated with the presence of both non-ionic and anionic groups in their molecules, a recent investigation of a phosphated nonylphenol ethoxylate demonstrated that the phosphate group had only a slight influence on the properties of this compound. The properties of an oil-soluble phosphated fatty alcohol ethoxylate of commercial origin has now been investigated. This material was substantially homogeneous, corresponding to a structure



Although with considerable solubility in non-polar solvents, the compound has a slight solubility in water which is increased with increased pH, suggesting that the polar phosphate group has an influence on the properties of the compound. Measurement of the surface tension of aqueous solutions over a temperature range of 20–50° showed that there was an inflection point in the relation between cmc and temperature, behaviour typical of an anionic surfactant. As the pH is increased, the interfacial cross-sectional area of the molecule is progressively reduced at the air-water interface, but increased at the hexane-water interface. These results are discussed in terms of the orientation of the molecule at the interface, and the influence of a charged polar head group.

Ethoxylated derivatives have been used as surfactants for some years but the introduction of a terminal phosphate group to the ethylene oxide moiety is a comparatively recent event (Nusselein, 1959). This class of materials is claimed (D. J. Tennant, private communication) to have properties associated with both the polyethylene oxide condensate and the anionic polar phosphate. In addition to being useful detergents, emulsifiers and stabilizers, they are stable in the presence of high concentrations of electrolyte over a wide range of pH.

They are usually supplied in the un-neutralized acidic form and when neutralized their low toxicity makes them useful as emulsifiers and stabilizers of pesticides and herbicides and may result in their application as wetting agents for pharmaceutical products.

We have recently investigated the properties of a phosphated nonylphenol ethoxylate (Groves, Mustafa & Carless, 1972) which behaved substantially as the corresponding nonylphenol ethoxylate, the terminal phosphate group apparently contributing little to the properties of the compound. This was attributed to the relative size of the ethylene oxide moiety which was large enough to determine the surface activity of the compound. It was therefore of interest to investigate a similar type of compound with a shorter ethylene oxide chain.

## MATERIALS AND METHODS

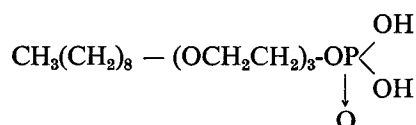
## Materials

Water, buffers and n-hexane—as described by Groves & others (1972).

*Phosphated fatty alcohol ethoxylate* (PFE): of commercial origin (Lankro Chemicals Ltd.), a straw coloured viscous liquid, readily soluble in non-polar solvents. When stored in vacuum over silica gel for 48 h it lost no weight at room temperature (20°). When heated at 105° there was a slight loss in weight after 48 h and a darkening in colour; heat at 150° resulted in slight charring. Only slight traces of free phosphoric acid could be detected in the material after dialysis through cellulose membranes against distilled water, and attempts to remove the free acid by precipitation with calcium chloride or by adsorption on to columns of mixed ion-exchange resins were not successful.

The surfactant has a refractive index of 1.4580 at 20° and no characteristic ultra-violet absorbance spectra. Thin layer chromatography on silica gel (E. Merck A.G., Darmstadt), according to Patterson, Hunt & Tucker (1966), produced only a single spot irrespective of the developing solvent system or the detection method employed (Groves & others, 1972). Measurement of the surface tension of aqueous solutions of the material showed that there was no significant depression of the curve; the concentration at the inflection point was associated with the critical micelle concentration (cmc) Fig. 1. Since these properties are consistent with the presence of only small quantities of homologous impurities the material was used as received.

The apparent average number molecular weight of the compound by vapour pressure osmometer (Mechrolab Model 301A) was 336 and a value of 354 was obtained by the Rast camphor method. Elemental analysis was C 55, H 10.3, P 5.8%, which is consistent with the claimed structure:



$\text{C}_{17}\text{H}_{33}\text{O}_5\text{P}$  requires C, 51.0, H 9.4 and P, 8.7%.

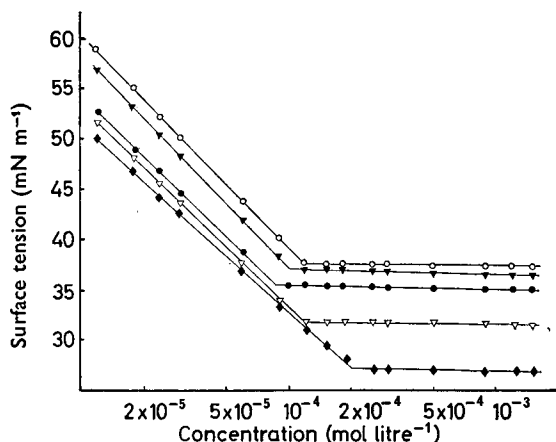


FIG. 1. Surface tension vs concentration curves of PFE in aqueous solutions at different temperatures ○ 20°, ▼ 25°, ● 30°, ▽ 40°, ◆ 50°.

## METHODS

*Surface and interfacial tensions* and *pH* were measured as described by Groves & others (1972).

*Aqueous solubility.* Variable amounts of the surfactant were added to constant volumes of water or aqueous buffer in sealed containers which were equilibrated at 20° with shaking for 48 h. The limit of solubility was indicated by turbidity of the solution and reported (Table 1) as the mean amount contained in adjacent tubes, one being clear and the other turbid.

Table 1. *The aqueous solubility of PFE at 20°.*

Substrate	pH	Concentration of a saturated solution mol litre <sup>-1</sup>
Water	3.4	0.0015
0.05M phthalate	4.01	0.0037
0.05M phosphate	6.88	0.0300
0.05M borate	9.22	0.1300

## RESULTS

Aqueous solutions of PFE are acidic, the pH falling with increased concentration. Titration with aqueous sodium hydroxide solution showed that the material had a  $pK_{a1}$  of 6.0 and  $pK_{a2}$  of 10.0.

The cmc in water was determined by surface tension measurements (Fig. 1) at different temperatures. The surface excess was calculated by the Gibbs adsorption equation, assuming the activities to be the same as concentrations, and from these results the cross-sectional areas were also calculated. (Fig. 2).

Measurement of the surface tension in the presence of 0.05 M buffer at 20° showed that the cmc was reduced when compared with unbuffered solutions. As the pH of the substrate was raised, there was a slight increase in cmc (Table 2). Calculation of the interfacial molecular cross-sectional areas under these conditions demonstrated that the area was progressively reduced as the pH was raised but, in the presence of hexane at the interface the opposite effect was observed (Table 2).

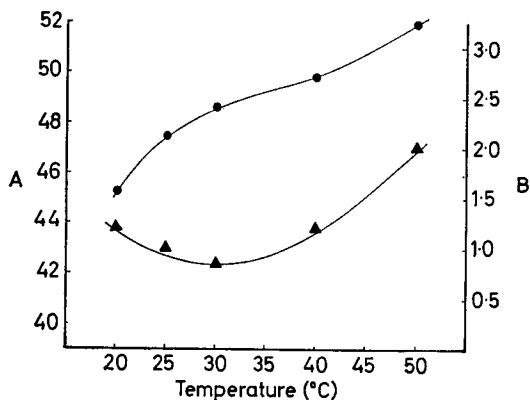


FIG. 2. The effect of temperature on the CMC and apparent cross-sectional area of the PFE molecule. A. Cross-sectional area ( $\text{nm}^2 \times 10^3$ ) ●. B. cmc ( $\text{mol litre}^{-3}$ ) ▲.

## DISCUSSION

That PFE is readily soluble in oils is hardly surprising in view of the predominance of the hydrophobic fatty alcohol moiety (Fine, 1958). However, the increase in the aqueous solubility with increase in pH suggests that the properties of the compound may be influenced by the terminal ionizable phosphate group. This is supported by the inflection in the cmc vs temperature curve (Fig. 2), which is a characteristic feature of anionic surfactants (Goddard & Benson, 1957). This feature is due to an initial desolvation of the monomer making it more hydrophobic. As thermal agitation increases cohesion between monomer molecules is decreased and the effect is reversed (Elworthy, Florence & Macfarlane, 1968). The increase of interfacial area with increase of temperature is slight (Fig. 2) but may also be attributed to increased thermal motion.

The effect of electrolytes on both the ionic and non-ionic surfactants is generally to lower the cmc, probably because of electrostatic screening action by salts, Becher (1967), Elworthy & others (1968). The addition of 0.05 M buffer salts at pH 4.01 lowered the cmc by an order of magnitude from that measured in water with an ambient pH of 3.4 (Table 2). Raising the pH to 9.2 resulted in an increase of cmc since, presumably, the terminal phosphate group ionizes and increases the electrostatic repulsion between monomer molecules.

Table 2. *The interfacial properties of PFE at 20°.*

Substrate	pH	cmc mol litre <sup>-1</sup> × 10 <sup>5</sup>	Apparent cross-sectional area nm <sup>2</sup> × 10 <sup>2</sup>	
			air-water	hexane-water
Water	3.4	12.00	45.2	—
0.05 M phthalate	4.01	2.3	89.5	88.0
0.05 M phosphate	6.88	2.7	74.5	91.2
0.05 M borate	9.22	3.5	65.1	102.0

The effective cross-sectional area of the molecule as measured by interfacial tension measurements is more accurately an area of disturbance around the molecule which prevents adjacent molecules from coming closer. The effective cross-sectional area of PFE shown in Table 2 is appreciably larger than that of a hydrocarbon chain and this is in agreement with the results of Elworthy & Macfarlane (1962) who found that a series of polyethoxylated hexadecyl alcohols at the air-water interface also had cross-sectional areas larger than that of a hydrocarbon chain,  $20.5 \times 10^{-2} \text{nm}^2$ . At the air-water interface PFE had an apparent cross-sectional area of  $45.2 \times 10^{-2} \text{nm}^2$  and in the presence of a buffer substrate this is increased from 65 to 90 according to the pH (Table 2).

The effect of pH on the formation of the charged polar phosphate group and the oxonium groups along the polyoxyethylene chain was discussed by Groves & others (1972) who suggested that the molecules might be capable of coiling, the thickness of the coil being determined by the environmental pH. However, in this case, since PFE has a short chain of three ethylene oxide units, this explanation does not seem likely and an alternative mechanism is required. The most likely explanation would seem to be in the manner in which the molecules are orientated along the interface

and this can be used to explain why the effects observed at the air-water interface are reversed at the hexane-water interface.

Since the greater part of the PFE molecule is 'oil-soluble' it would be anticipated that in the acid state when the terminal polar group is unionized and there is some formation of the weakly charged oxonium groups in the polyethylene oxide moiety, the molecule would lie in a plane substantially parallel to the hexane-water interface with the fatty alcohol portion being in the oil and the slightly polar portion being orientated towards the water surface. In the case of the air-water interface the molecule must lie along the interface and this is suggested by the fact that the cross-sectional areas for both types of interface are very similar at pH 4 (Table 2).

As the pH of the aqueous substrate is increased the terminal phosphate groups ionize and increase the electrostatic repulsion between the molecules. The net result is to increase the separation and an apparent increase in the cross-sectional area of the molecule (Table 2).

Thus, in contrast to the previously investigated compound which has 8-9 ethylene oxide units and behaves substantially as a non-ionic surfactant, PFE has properties which are dominated by the terminal anionic phosphate group.

#### *Acknowledgements*

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